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## OZONE REMOVAL METHOD

### CLAIM(S)

- 1) An ozone removal method characterized in that the ozone-containing gas is brought into contact with an active carbon impregnated with active manganese oxide.
- 2) An ozone removal method, as cited in Claim 1, wherein one or more types of alkali metal and/or alkali earth metal are impregnated in the active carbon as a secondary component.

### DETAILED DESCRIPTION OF THE INVENTION

The present invention pertains to a method to efficiently remove ozone from an ozone-containing gas.

Ozone, for its having powerful oxidation power, is widely used for purification and sterilization of water, treatment of waste from plants, treatment of sewage water, flue gas denitrification, and removal of hostile odor.

Taking into account the following factors, it is pretty obvious that the ozone usage will be increased in various fields: ozone can be generally manufactured by a simple operation using air or oxygen as a raw material; ozone is sufficiently reactive to phenol cyan in water, hydrogen sulfide, which is a hostile odor component in the air, mercaptan group or nitrogen oxides in exhaust gases.

With the systems related to ozone in general, an excessive amount of ozone needs to be used to completely perform an oxidation reaction. As a result, non-reacted ozone is vented out.

As is publicly known, ozone causes air pollution therefore is an oxidant generation substance. It negatively affects human bodies, destroys chlorophyll of farm products, causing a problem of reducing assimilation, so excessive ozone needs to be removed to prevent a secondary pollution. Accordingly, it has been demanded to quickly develop economical and high performance ozone removing treatment, so an active carbon method, a thermal cracking method, and a chemical solution absorbing method have been proposed up to now. A thermal cracking method is a method to thermally decompose ozone by a burner of heavy oil and light oil; an ozone-containing gas is introduced into a decomposing furnace of 300 – 400°C and

the ozone is decomposed. The ozone concentration in the gas is low, so the method is not economical for its heating a high volume of air.

A chemical solution absorbing method is a method to absorb ozone by introducing an ozone-containing gas into a reducing agent solution, such as a ferrous solution, a sulfurous acid soda, and a thiosulfite soda, or into an alkaline solution such as a caustic soda. This method, however, comes with the problems that the absorbing performance declines by a change of chemical solution composition by the ozone absorbing and addition of chemical agent, that the method cannot handle the change in concentration of ozone in the gas (The tracking performance relative to a load change of ozone-containing gas is poor.), and that the waste treatment is not possible.

An active carbon method is a method to introduce an ozone-containing gas into particulate active carbon layer to decompose oxygen on the surface of active carbon. This method is excellent in tracking down the load changes of ozone-containing gas and has an advantage of decompose/remove very low-concentration ozone at a normal temperature but has a disadvantage that an air pressure loss is high; the active carbon is oxidized and lost, which then needs to be added.

The decomposition mechanism of ozone by an active carbon is complex, but it is primarily divided into three functions: 1) ozone

adsorption function (in narrow sense); 2) ozone decomposition catalytic function; 3) chemical reaction of active carbon to oxygen atom decomposed by ozone. In the past, it was considered that by the ozone treatment using an active carbon, about 5 gram of ozone can be treated by 1 gram of active carbon. Since the aforementioned three functions are interlaced with complexity and the condition under which ozone and active carbon are contacting with each other has a large impact on these functions, so the ozone decomposing mechanism of active carbon cannot be explained simply by their stoichiometric relationship.

The inventors studied with a focus on the chemical effect of ozone at a normal temperature and found that the ozone absorbance into an active carbon has a great impact on ozone decomposition and active carbon useful life at a relatively low temperature such as a normal temperature. More specifically, at a relatively low temperature, ozone is adsorbed into active carbon at a considerable ratio in parallel to the catalytic function. If the absorbed ozone is quickly decomposed and separated, the active points will not be lost, and the active carbon will not lose its activity. But due to ozone's strong oxidation power, a composite body of C<sub>m</sub>O<sub>n</sub> (m/n : 1 – 2) consisting of carbon and oxygen is formed on the surface of active carbon. This composite body is not separated but is gradually accumulated on the

active carbon surface and covers the active points, undercutting the ozone decomposing activity. Based on this new discovery, the inventors continued the research and found that when the active carbon impregnated with active manganese oxide, ozone in the gas is very effectively decomposed on its surface and that the active carbon impregnated with an alkali metal or one or more alkali earth metals as a second component provides high decomposing performance and increases the useful life of active carbon by 3 – 4 times; thereby produced the present invention.

Accordingly, the present invention presents an ozone removal method characterized by that an ozone-containing gas is brought into contact with an active carbon impregnated with active manganese oxide.

For the active carbon used for the present invention, anything can be used as long as it is made of charcoal, coke, and palm, and is activated by a conventional method. Its surface dimension is preferably about 700-2000m<sup>2</sup>/g. Its shape may be particulate form, pulverized form, or any form. Particularly, the palm material crushed into active carbon is preferred. In this invention, the active carbon is impregnated with active manganese oxide. The active manganese oxide is expressed by MnO<sub>x</sub> (x = 1, 3 – 2.0). The active carbon is produced by impregnating it with manganese compounds, such as manganese chloride, nitrate, acetate, thiocyanate,

phosphate, and carbonate, and subsequently by heating at about 100 - 500°C, more preferably, at about 150 - 250°C in a flow of inactive gas, e.g., nitrogen, carbon dioxide, and helium.

The impregnated amount of active manganese oxide is about 0.1 – 10 weight% of Mn, more specifically, 0.5 – 5 weight%, is preferred.

The means of impregnating the active manganese oxide may be any means, for example, they are: 1) After a water-soluble manganese compound is dissolved in water, this solution is impregnated into the active carbon, followed by drying and sintering; 2) A water-insoluble manganese compound is mixed in the active carbon in the process of manufacturing the active carbon.

It is also possible to impregnate an alkali metal and/or two or more alkali earth metals. In case of impregnating an alkali metal, for example, hydroxide of sodium and potassium or nitrate is dissolved in water, and this solution is impregnated in the active carbon, followed by drying and sintering. In case of impregnating an alkali earth metal, for example, chloride, bromide, iodide, or nitrate of calcium, strontium, barium, and radium is dissolved in water, and subsequently the solution is impregnated in the active carbon by the means mentioned in (1). In case of carbonate, nitrate, fluoride or phosphate of the aforementioned element are

impregnated, these compounds are mixed in the material of active carbon by the aforementioned means (2). As for the amount to be impregnated, provided that the amount of alkali metal and/or alkali earth metal element is M and the amount of active manganese oxide is Mn, the sum of Mn and M preferably does not exceed about 10 weight%.

The ozone-containing gas is brought into contact with the active carbon thus manufactured. The amount of ozone contained in the ozone-containing gas may be at any level of concentration, but about 1 ppm-10,000 ppm is preferred. The contacting temperature is preferably as low as possible, and 0 - 60°C is preferred. The duration of contact is generally about 1/10 –20 seconds, particularly, about 1/5 – 10 seconds. When the gas is brought into contact with these active carbon, is used a publicly-known method, for example, a fixed bed, movable bed, fluidity bed, slurry method, or batch method. The active carbon used for the present invention is highly activated relative to the prior art one and has a longer useful life, so its use amount can be about 1/3 –1/4 the about of the prior art one. Therefore, by the present invention, the active carbon charging tower is made smaller and air permeation resistance in the active carbon charged layer is lower. This allows the lower construction cost for the device and the lower cost for operation, which is economically advantageous. The present invention is

explained below more specifically with reference to the embodiment example and comparative example.

### Embodiment Example 1

To the crushed palm active carbon with BET surface dimension 1050 m<sup>2</sup>/g and grain size 9 – 14 mesh, 3 weight% of manganese nitrate solution was sprayed and heated in 200°C nitrogen flow for about 1 hour to manufacture the active carbon containing 1 weight% of Mn. The activity test of ozone decomposition was conducted under the following parameters by using the active manganese oxide-impregnated carbon thus produced, and the result is shown in Table 1.

Catalytic layer: 0.65 cm Ø x 4.5 cm (capacity 1.5 ml)

Reaction temperature: 25°C

Total gas flow rate: 1.0 l/min

Gas composition: Air containing ozone 80 ppm and relative humidity 50%

### Embodiment Example 2

To the crushed palm active carbon with BET surface dimension 1050 m<sup>2</sup>/g and grain size 9 – 14 mesh, a solution containing 3 weight% of manganese acetate and 1 weight% of magnesium chloride was sprayed and heated in 200°C nitrogen flow for about 1 hour to produce an active carbon containing 0.7 weight% of Mn and 0.2 weight% of Mg. By using thus

produced active carbon impregnated with manganese and magnesium, the ozone decomposing activity test was conducted likewise as in Embodiment Example 1, and the result is shown in Table 1.

#### Comparative Example 1

The crushed palm active carbon having BET surface dimension 1050 m<sup>2</sup>/g and grain size 9 – 14 mesh was dried in 110°C nitrogen atmosphere for about 1 hour, and subsequently, the ozone decomposing activity test was conducted as in Embodiment Example 1. The result is shown in Table 1.

Table 1 Ozone decomposing performance

|                       |   | Ozone decomposition rate (%) |                |                |                |
|-----------------------|---|------------------------------|----------------|----------------|----------------|
|                       |   | After 10 hours               | After 20 hours | After 30 hours | After 40 hours |
| Embodiment Example 1  | The active carbon was impregnated with Mn 1.0 weight%.                    | 100                          | 100            | 80             | 70             |
| Embodiment Example 2  | The active carbon was impregnated with Mn 0.7 weight% and Mg 0.2 weight%. | 100                          | 100            | 100            | 94             |
| Comparative Example 1 | Active carbon alone   | 50                           | 46             | 45             | 40             |

#### Embodiment Example 3

When preparing the active carbon out of coal material, manganese nitrate and calcium carbonate were added, and by a conventional manufacturing method, was manufactured an active carbon containing 0.2 weight% of Mn and 1.9 weight% of Ca and having the BET surface dimension 1200 m<sup>2</sup>/g and grain size 4 – 6 mesh. The active carbon impregnated with manganese and calcium thus prepared was pulverized to

grain size 8-16 mesh, and the ozone decomposing activity test was conducted under the following parameters. The result is shown in Table 2.

Catalytic layer: 0.65 cm Ø x 9.0 cm (capacity 3.0 ml)

Reaction temperature: 25°C

Total gas flow rate: 1.0 l/min

Gas composition: air containing ozone 40 ppm and having relative humidity 50%.

#### Embodiment Example 4

A market-purchased palm active carbon for air cleaning having BET surface dimension 126 m<sup>2</sup>/g and grain size 4 – 6 mesh was pulverized to 8 – 16 mesh and was immersed in a solution containing manganese nitrate by 2 weight% and sodium nitrate by 1 weight% for about 10 hours. After the solution was separated, the active carbon was heated in 150°C nitrogen flow for about 1 hour to manufacture the active carbon containing 0.8 weight% Mn and 0.5 weight% Na. The ozone decomposing activity test was conducted as in Embodiment Example 3 by using the active carbon impregnated with manganese and potassium. The result is shown in Table 2 below.

### Comparative Example 2

The market-purchased palm active carbon for air cleaning having the surface dimension 1260 m<sup>2</sup>/g and grain size 4 –6 mesh was pulverized to 8 – 16 mesh. The ozone decomposing activity test was conducted by using this active carbon. The result is shown in Table 2.

### Comparative Example 3

To a market-purchased silica alumina with BET surface dimension 225 m<sup>2</sup>/g and average grain size 2m/m, a solution containing 5 weight% of potassium permanganate was sprayed and heated in 250°C nitrogen flow for about 1 hour to manufacture silica alumina impregnated with potassium and manganese that contains 1.2 weight% of Mn and 0.7 weight% of K. The ozone decomposing activity test was conducted by using the silica alumina thus produced, as in Embodiment Example 3. The result is shown in Table 2 below.

Table 2 Ozone decomposing performance

|                       |   | Ozone decomposition rate (%) |                 |                 |                 |
|-----------------------|---|------------------------------|-----------------|-----------------|-----------------|
|                       |   | After 100 hours              | After 200 hours | After 300 hours | After 400 hours |
| Embodiment Example 3  | Active carbon impregnated with Mn 0.2 weight % and Ca 1.9 weight% | 100                          | 100             | 100             | 92              |
| Embodiment Example 4  | Active carbon impregnated with Mn 0.8 weight% and Na 0.5 weight%  | 100                          | 100             | 100             | 100             |
| Comparative Example 2 | Active carbon alone   | 100                          | 56              | 43              | 25              |
| Comparative Example 3 | Silica alumina impregnated with Mn 1.2 weight% and K 0.7 weight%  | 13                           | 3               | 0               | -               |

As is evident from the above table, the active carbon used in the present invention has a high capability of decomposing the ozone contained in the ozone-containing gas and has a long useful life.

Translations

U. S. Patent and Trademark Office

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